

UK Patent Application (12) GB (19) 2 279 359 (13) A

(43) Date of A Publication 04.01.1995

(21) Application No 9313066.4

(22) Date of Filing 24.06.1993

(71) Applicant(s)

Unilever Plc

(Incorporated in the United Kingdom)

Unilever House, Blackfriars, LONDON, EC4P 4BQ,  
United Kingdom

(72) Inventor(s)

Caroline Susan Cordery

Alfred Roy Elmes

Ezat Khoshdel

(74) Agent and/or Address for Service

S R Bristow

Unilever Plc, Patent Division, Colworth House,  
Sharnbrook, BEDFORD, MK44 1LQ, United Kingdom

(51) INT CL<sup>6</sup>

C08B 37/08, A61K 7/06 7/11

(52) UK CL (Edition N)

C3U UDE U205 U319 U406 U419 U506 U522 U524

U525 U529

D1P PE P1107 P1207 P1256 P1257 P1272 P1296 P1312

P1314

U1S S1124

(56) Documents Cited

None

(58) Field of Search

UK CL (Edition L) C3U UDE

INT CL<sup>5</sup> A61K, C08B

ONLINE DATABASES: WPI

(54) Fibre treatment materials and compositions containing them

(57) A salt of Chitosan or a chitosan derivative with one or more molecules of a hydroxycarboxylic acid having a carbon chain backbone with a length of at least 5 carbon atoms and containing at least one hydroxyl group. Also a composition including the salt and a method for treatment of fibres with the composition.

GB 2 279 359 A

FIBRE TREATMENT MATERIALS AND COMPOSITIONS  
CONTAINING THEM

This invention relates to materials and compositions containing them which impart a combination of tactile benefits to fibres such as hair, natural or synthetic textiles or other fabric materials. The invention relates particularly to materials and compositions containing them which impart a combination of fibre conditioning and setting (i.e. increased hold and/or body) attributes.

The use of conditioning compositions for imparting smoothness, softness and other tactile and/or visual benefits to fibres such as hair is well known and many materials have been identified which are able to deliver such benefits, thereby finding use in hair conditioning compositions, fabric conditioners, softeners and like products.

One particular range of materials which have hitherto been proposed for inclusion in conditioning compositions are 2-hydroxyalkanoic acids, as described in EP-A-0403303. These materials, for example 2-hydroxy octanoic acid (also known as hydroxycaprylic acid, HCA) deliver improved elasticity to hair fibres. Other conditioning agents for use on hair and other fibres are well known in the literature and include film-forming polymetric materials such as polyvinyl pyrrolidone, polyvinyl acetate, polymers derived from acrylic acid or derivatives thereof, cellulose derivatives, natural gums and resins and various silicones, which are typically useful for imparting a combination of conditioning benefits such as

smoothness, softness and ease of combing when applied to hair.

For the purpose of giving hair greater body and hold and to increase its ability to hold a given style, another range of materials which are known for inclusion in hair treatment compositions are certain complexes or salts of chitosan and chitosan derivatives. Chitosan is a deacetylation product of chitin, a natural polyglucosamine whose amine groups are acetylated, and is found in the shells of crustacea and in certain insects, as well as in some fungi and algae where it may be found in complexed form.

Known salts of chitosan or chitosan complexed with a glycan are disclosed in the art as being useful in hair styling compositions for imparting good hold and superior style retention to hair. In the case of water soluble salts of chitosan-glycan complexes, this is especially so under conditions of high humidity, as disclosed in EP-A-0403282.

More generally, there are several disclosures in the art of chitosan salts with certain acids for use as film-forming components in hair setting compositions. US-A-4134412 (corresponding to GB-A-1583086) discloses water-soluble salts of chitosan for hair setting, the salts being those of various acids of which the preferred ones are formic, acetic, or lactic acids. We have found however that in particular acetic acid gives a chitosan salt which, when applied to fibres such as hair, gives such a strong bodying effect that hair properties such as smoothness and softness are severely damaged, such that the material is of little practical value in a realistic fibre treatment product such as for use on hair.

International Conference Proceedings", 1982, Pub. Japan Soc. Chitin, Chitosan (Ed. Hirano), Pages 205-209, "Investigations on Chitosan as a Natural Film-Forming Ingredient in Hair Cosmetic Products under the Consideration of Ecological Aspects", reports solubilities of chitosan in various aqueous acids for the purpose of producing film-forming solutions, among which acids are mentioned a wide variety of organic carboxylic acids, notably various hydroxy acids, dicarboxylic acids and some amino acids. The paper concludes that such salts of chitosan can be used to good effect for improving the permanence and set of hair, for example in place of conventional synthetic hair setting polymers such as polyvinylpyrrolidone/vinylacetate-based materials. The paper does not however address the question of the condition of hair treated with the disclosed salts and moreover we have found, as mentioned above, that some of the disclosed acids, e.g. acetic acid, give rise to materials having little practical usefulness in consumer-acceptable products, owing to their over-excessive fibre setting properties.

Up to now there have been few practical attempts at producing treatment compositions for hair or other fibres which simultaneously provide conditioning as well as bodying/styling benefits. A major factor in this lack of prior art teaching may be that these two attributes are generally considered to be mutually exclusive, in the sense of being opposite extremes of an overall quality/managability of the hair or other fibres in question, such that an attempt to attain a combination of both types of benefit simultaneously and each at a useful level would be expected to lead to an unsatisfactory compromise of both.

There have however recently been some proposals for hair treatment compositions which simultaneously

provide some conditioning benefit as well as some increased hold/styling benefit. For example, EP-A-240350 discloses hair care compositions which give both improved style retention and hair conditioning properties, and comprise certain silicone polymers which have a particular defined high complex viscosity, together with a volatile carrier. It is not entirely clear from the disclosure, however, whether or not the combined styling and conditioning benefits are derived from the rigid silicone polymer alone or from the combination of defined essential ingredients.

As a result of extensive investigations into possibilities for manufacturing from known conditioning materials and bodying/styling materials new materials which when applied to hair or other fibres result in good performance both as regards conditioning and bodying/setting, we have surprisingly found a family of new materials which when applied to fibres such as hair can impart both of these benefits simultaneously and to an excellent degree.

Accordingly, in a first aspect the present invention provides a salt of chitosan or a chitosan derivative with one or more molecules of a hydroxycarboxylic acid having a carbon chain backbone with a length of at least about 5 carbon atoms and containing at least one hydroxyl group.

In a second aspect, the invention provides a fibre conditioning and bodying/setting composition comprising a salt of chitosan or a chitosan derivative with one or more molecules of a hydroxycarboxylic acid having a carbon chain backbone with a length of at least about 5 carbon atoms and containing at least one hydroxyl group.

In a further aspect, the invention provides a

method of treating fibres to simultaneously condition them and give them enhanced body and hold, the method comprising treating the fibres with the above-defined composition in accordance with the invention.

In yet a further aspect of the invention, there is provided the use of the above-defined salts or compositions containing them for treating fibres to simultaneously condition them and give them enhanced body and hold.

The various aspects of the invention and preferred embodiments and features thereof will now be described in detail.

#### Chitosan-hydroxycarboxylic acid salt

The chitosan-hydroxycarboxylic acid salts which form the basis of the present invention are characterised by having at least one carboxylic acid moiety having a relatively long carbon chain backbone, which may be linear or branched or possibly even cyclic and including at least one hydroxyl group, preferably from one to about five hydroxyl groups, more preferably one, two or three hydroxyl groups. The hydroxyl group or groups may be situated anywhere on the carbon chain, but preferably at least one of them is near the carboxy functional group of the acid moiety, especially at the 2-position relative thereto.

Preferably, the chitosan-acid salts of the invention are water-soluble (at ambient temperature), in order that they may be readily incorporated in and form films when deposited from conditioning and bodying/setting compositions which comprise one or more volatile solvents such as water and/or alcohols, especially lower alcohols, e.g. ethanol, propanol. Deposition of the chitosan-acid salts of the invention

may be for example by evaporation of such solvents from the composition applied to the fibres to be treated, or alternatively, and preferably, and especially in the case of hair, may be by means of conventional deposition technology, in which case (though whilst not intending to be bound by theory) the solubility of the salts may not be so important.

As a starting material for preparing the chitosan-acid salts of the present invention, any suitable commercial source of chitosan may be used. Methods for the preparation of chitosan from natural sources such as crustacea and various microorganisms are well documented in the patent literature.

Suitable commercial sources of chitosan include for example Fluka low molecular weight chitosan (mwt. about 70,000), Sigma crabshell-derived chitosan (quoted molecular weight  $0.5-2.5 \times 10^6$ ) and Amerchol Chitosan M (mwt. about 300,000).

Within the scope of the present invention, derivatives of chitosan may be used to form the chitosan-acid salts. Such derivatives may be for example complexes of chitosan with a glycan, i.e. through complexation at one or more free hydroxyl groups and/or amine groups in the chitosan moiety, or alternatively an N-derivatised chitosan such as those derivatives disclosed in US 4780310.

As the acid component of the chitosan salts of the invention, a wide range of acids may be suitable. Preferred acids are those having a linear or branched carbon chain backbone with a length of at least about 5 or 6, preferably from about 5 to about 30, more preferably from about 5 to about 20, especially from about 6 to 16, carbon atoms, the carbon chain being preferably unsaturated but optionally containing one or

more unsaturated groups and possibly including a cyclic moiety as at least part of the carbon chain. The acid moiety preferably contains from one to about five hydroxyl groups, more preferably from one to about two or three hydroxyl groups. Where only a low number such as one or two hydroxyl groups are present, they are preferably situated proximal to, i.e. at least one at the 2-position relative to, the carboxy functionality, thereby forming in preferred embodiments a substantially hydrophobic alkyl chain forming the remainder of the acid moiety.

Preferred acids are monocarboxylic acids. Acids containing more than one carboxyl group are also possible, but preferably the number of carboxyl groups in the molecule is selected to be sufficiently low, and the distribution of carboxyl group in the molecule controlled, so as to avoid the tendency for the acid to cross-link with other reactive groups in the chitosan molecule, or alternatively with other chitosan molecules, thereby forming water-insoluble products which may be less preferred for use in compositions in accordance with the invention.

A particularly preferred group of acids for forming salts with chitosan in accordance with the invention are 2-hydroxyalkanoic acids, especially those containing from about 6 to about 12 or 14 carbon atoms. A particularly preferred example is 2-hydroxyoctanoic acid (HCA), which forms a chitosan salt having especially good fibre conditioning and bodying/setting properties and is especially useful in hair conditioning and styling/setting compositions of the invention.

Further suitable acids for use in the invention include for example: relatively long chain polyhydroxy carboxylic acids, such as gluconic acid, glucuronic acid; fatty acids containing at least one hydroxyl



group.

Within the scope of the present invention are mixed chitosan-acid salts, wherein the material comprises the product of the reaction of chitosan with at least one of the above-defined essential hydroxycarboxylic acids and also a secondary acid which may be any suitable known acid. In this context the secondary acid may for example be an acid already known in the art for salt formation with chitosan for the production of film-forming materials, or it may be some other acid having suitable reaction properties and lending appropriate overall properties to the final mixed salt product. Examples of suitable secondary acids include acetic acid, amino acids, other hydroxycarboxylic acids and saccharide-derived acids, e.g. lactobionic acid.

The use of a secondary acid, such as a short chain monocarboxylic acid, e.g. acetic acid, in combination with the essential acid characteristic of the invention is particularly useful for rendering such otherwise water-insoluble acids soluble for incorporation in the form of aqueous solution in treatment compositions according to the invention.

The novel chitosan salts of the invention may be prepared by simple low temperature reaction protocols, for example by simply adding the chitosan (e.g. in dry powder form) to a preferably aqueous solution of the appropriate acid. Depending upon the solubility of the acid and/or the chitosan in the medium in which the reaction is effected, additional acid, e.g. acetic acid or a strong inorganic acid, may be added to the solution in order to achieve dissolution of the reagent(s).

The chitosan starting material used in the salt

preparation is preferably first hammer milled to reduce the particle size to the order of about 1mm or less. Smaller particle sizes facilitate more rapid dissolution of the chitosan in the aqueous acid.

The quantities of chitosan and acid used to prepare the salts with the invention are preferably equimolar with respect to each other, allowing for the degree of deacetylation of the chitosan, for example 85% of the theoretically required amount of acid is preferably used if the chitosan is 85% deacetylated. In this case, the degree of deacetylation will be apparent from the commercial chitosan source or readily determinable by persons skilled in the art from the manner of manufacture of the chitosan in question.

The initially formed suspension of chitosan in aqueous acid may be gently stirred with some warming if necessary, until as much chitosan as possible (preferably at least about 90%) has dissolved to give a somewhat viscous, clear solution. The pH of the solution may be adjusted as required, and is preferably in the range of from about 5 to about 6. As already mentioned above, a lower pH may be desirable for achieving adequate dissolution of the starting materials.

In order to remove any remaining chitosan particles which remain undissolved, the solution may be sieved or filtered and may then be used directly in the production of a fibre treatment composition which contains the salt as a primary active ingredient. Alternatively, the solution of the salt may be freeze-dried by conventional means to obtain a dry chitosan-acid salt product. As a further alternative, conventional precipitation techniques, followed by washing and drying, may be employed, although freeze-drying is the more preferred method of forming a dry

product for future use, because it generally results in a product which has a higher water solubility than for example precipitated monoliths.

Evidence for the existence of true chitosan acid salts of the invention, as opposed to mere mixtures of the two components, has been obtained by NMR studies as well as other observations on their physical behaviour. Without intending to be limited by theory or specific physical parameters, the following observations have been found to be relevant:

- (a) with chitosan salts of 2-hydroxycarboxylic acids,  $^1\text{H}$  NMR spectra of the salts show an upfield chemical shift of 0.2 to 0.3ppm of the proton(s) in the 2-position to the carboxylate carbon atom in the salt, with respect to the chemical shift value in the free, uncomplexed acid. For example, for free 2-hydroxycaprylic acid in  $\text{D}_2\text{O}$ ,  $\delta$  ( $\alpha$ -proton) = 4.22ppm, whereas for the chitosan - 2-hydroxycaprylic acid complex,  $\delta$  ( $\alpha$ -proton) = 4.02ppm.
- (b) Chitosan dissolves in a 1-2% aqueous solution containing a molar equivalent of the particular acid. Chitosan alone is not water-soluble.
- (c) Free chitosan precipitates out from aqueous acid solution when base is added and the pH raised to above 7.

Fibre treatment compositions in accordance with the invention

Fibre conditioning and bodying/styling/setting

compositions in accordance with the present invention comprise one of more species of chitosan-acid salt of the invention, preferably together with one or more conventional ingredients as normally found in prior art treatment compositions for use in similar regimes on the same or similar types of fibre.

The compositions in accordance with the invention are preferably aqueous and may contain from about 0.01 to about 40% by weight of the chitosan-acid salt, preferably from about 0.05 to about 20%, even more preferably from about 0.1 to about 10% by weight, of the total composition. In general, the exact amount of the salt utilised may depend upon the degree of conditioning and/or bodying/setting provided by the salt in question, and/or the degree of conditioning and/or bodying/setting desired to be imparted to the fibres to be treated. Suitable amounts of salt may be readily determinable by practical experience or trial and error.

In addition to the chitosan-acid salt, the compositions of the invention may include one or more additional ingredients, depending for example on the intended use and physical form of the final composition.

Particularly preferred compositions in accordance with the invention are compositions for treating the hair, which may be in the form of shampoos, conditioners, lotions, gels, mousses, or the like.

Particularly in the case of compositions of the invention which are in the form of shampoos, i.e. compositions for simultaneously cleaning, conditioning and styling the hair (which are particularly preferred embodiments of the composition of this invention), the composition preferably comprises one or more surfactants, preferably selected from anionic, non-

ionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

Suitable anionic surfactants are the alkyl sulphates, alkyl ether sulphates, alkaryl sulphonates, alkanoyl isethionates, alkyl succinates, alkyl sulphosuccinates, N-alkoyl sarcosinates, alkyl phosphates, alkyl ether phosphates, alkyl ether carboxylates, and alpha-olefin sulphonates, especially their sodium, magnesium, ammonium and mono-, di- and triethanolamine salts. The alkyl and acyl groups generally contain from 8 to 18 carbon atoms and may be unsaturated. The alkyl ether sulphates, alkyl ether phosphates and alkyl ether carboxylates may contain from 1 to 10 ethylene oxide or propylene oxide units per molecule, and preferably contain 2 to 3 ethylene oxide units per molecule.

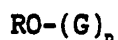
Examples of suitable anionic surfactants include sodium oleyl succinate, ammonium lauryl sulphosuccinate, ammonium lauryl sulphate, sodium dodecylbenzene sulphonate, triethanolamine dodecylbenzene sulphonate, sodium cocoyl isethionate, sodium lauroyl isethionate and sodium N-lauryl sarcosinate. The most preferred anionic surfactants are sodium lauryl sulphate, triethanolamine lauryl sulphate, triethanolamine monolauryl phosphate, sodium lauryl ether sulphate 1EO, 2EO and 3EO, ammonium lauryl sulphate and ammonium lauryl ether sulphate 1EO, 2EO and 3EO.

Nonionic surfactants suitable for use in compositions of the invention may include condensation products of aliphatic ( $C_6-C_{18}$ ) primary or secondary linear or branched chain alcohols or phenols with alkylene oxides, usually ethylene oxide and generally having from 6 to 30 ethylene oxide groups.

Other suitable nonionics include mono- or di-

alkyl alkanolamides. Examples include coco mono- or di-ethanolamide and coco mono-isopropanolamide.

Further suitable nonionic surfactants are the alkyl polyglycosides (APG's). Typically, the APG is one which comprises an alkyl group connected (optionally via a bridging group) to a block of one or more glycosyl groups. Preferred APG's are described by the following formula:



wherein R is a branched or straight chain alkyl group which may be saturated or unsaturated and G is a saccharide group.

R may represent a mean alkyl chain length of from about  $C_5$  to about  $C_{20}$ . Preferably, R represents a mean alkyl chain length of from about  $C_8$  to about  $C_{12}$ . Most preferably the value of R lies between about 9.5 and about 10.5. G may be selected from  $C_5$  or  $C_6$  monosaccharide residues or mixtures of  $C_5$  and  $C_6$  monosaccharide residues, and is preferably a glucoside. G may be selected from the group comprising glucose, xylose, lactose, fructose, mannose and derivatives thereof. Preferably G is glucose.

The degree of polymerisation n, may have a value of from about 1 to about 10 or more. Preferably, the value of n lies in the range of from about 1.1 to about 2. Most preferably the value of n lies in the range of from about 1.3 to about 1.5.

Suitable alkyl polyglycosides for use in the invention are commercially available and include for example those materials identified as: Oramix NS10 ex Seppic; Plantaren 1200 and Plantaren 2000 ex Henkel.

Amphoteric and zwitterionic surfactants suitable for use in compositions of the invention may include alkyl amine oxides, alkyl betaines, alkyl amidopropyl betaines, alkyl sulphobetaines (sultaines), alkyl glycinate, alkyl carboxyglycinates, alkyl amphopropionates, alkylamphoglycinates alkyl amidopropyl hydroxysultaines, acyl taurates and acyl glutamates, wherein the alkyl and acyl groups have from 8 to 19 carbon atoms. Examples include lauryl amine oxide, cocodimethyl sulphopropyl betaine and preferably lauryl betaine, cocamidopropyl betaine and sodium cocamphopropionate.

The surfactant(s) may be present in the cosmetic compositions of the invention in a total amount of from about 1 to about 40% by weight, preferably from about 2 to about 30% by weight.

Water and/or other conventional solvents, e.g. a lower alcohol such as ethanol, is another preferred component of the compositions of the invention and may be present in an amount of from about 5 to about 99% by weight, preferably from about 20 to about 80% by weight, of the total composition.

If desired, the compositions of the invention may comprise, in addition to the essential novel chitosan-acid salts of this invention, a minor amount of one or more other chitosan-acid salts already known in the art for use as film-forming materials, examples of which are mentioned in the prior art references acknowledged hereinabove. It is furthermore possible to include in the compositions as a secondary film forming ingredient a salt of chitosan with an acid as mentioned above in the context of secondary acids which may be used to form mixed salts in accordance with the invention.

If desired, for example depending upon the

overall level of fibre conditioning inherent in the particular chitosan-acid salt of the invention which is used, the compositions of the invention may contain one or more additional conditioning agents, such as those included in conventional fibre conditioning compositions. Suitable conditioning agents include cationic surfactants, cationic polymers, quaternised silicones, volatile and non-volatile silicones, protein hydrolysates, quaternised protein hydrolysates, and mixtures thereof. Examples of such materials are widely described in the patent literature and commercially readily available. Suitably, an amount of any additional conditioning agent present will be determined by the overall degree of conditioning performance required of the composition.

Similarly, if desired, for example depending upon the overall level of fibre bodying/hold/setting inherent in the particular chitosan-acid salt of the invention which is used, the compositions of the invention may contain one or more additional bodying/hold/setting agents, such as those conventional film-forming polymers included in known fibre treatment compositions of this type, examples of which are mentioned herein and will be well known to those skilled in the art. Suitably, an amount of any additional bodying/hold/setting agent present will be determined by the overall degree of such performance required of the composition.

The compositions of the invention may also comprise other conventional adjunct materials known for use in cosmetics or fibre treatment compositions, including for example suspending agents, thickeners, pearlescing agents, opacifiers, salts, perfumes, buffering agents, colouring agents, emollients, moisturisers, foam stabilizers, sunscreen materials, antimicrobial agents, preservatives, natural oils and extracts, propellants.



### Product form and use

The fibre treatment compositions of the invention may be formulated and provided in appropriate form for use on the hair, i.e. as hair conditioning and styling compositions, or for use on fabrics and textile materials, i.e. as fabric conditioning and bodying compositions.

Physical product forms and protocols for use may typically be the same as prior art products of these types.

Hair treatment compositions in accordance with the present invention may be provided in the form of shampoos, conditioners or styling, setting, shaping or blow-drying products and may take the form of low to moderate viscosity liquids, lotions, gels, creams, mousses or sprays. Due to their being able to form coherent, non-tacky, transparent, flexible, smooth and soft films on fibres treated with them, the chitosan-acid salts of the invention result in excellent conditioning attributes such as smoothness and softness, whilst at the same time giving good hold, bodying, setting or styling benefits when applied to hair.

Similar combined benefits are attainable with fibres other than hair, e.g. natural or synthetic fabrics, e.g. wool. Particularly in the context of wool treatment the invention provides a further benefit, namely that of anti-pilling.

A further advantage of the chitosan-acid salts of this invention is that they have been found to exhibit useful antimicrobial activity, for example against yeasts and Gram positive and Gram negative bacteria.

The invention will now be further illustrated by way of the following non-limitative Examples. These Examples demonstrate the advantageous effects of the invention on hair fibres, this being the most readily available and reliable way of assessing the combined benefits characteristic of the materials and compositions of the invention. However, it will be appreciated that similar results are attainable with other fibres such as wool and other fibrous materials, for example fabrics and textiles.

#### Examples

In the following Examples, the methods used for measurement of hair curl retention, body, smoothness and ease of comb were as follows:

##### Curl retention

For each product to be tested three Yugo Red Tie hair switches were used, 1 gm, 23 cm. A Hellermann sleeve was attached with Araldite 1 cm from the root end. The switches were then soaked in 1.6% (w/w) SLES 2EO for 2 hours. After this time they were removed and rinsed using tap water until all foam was removed (approximately 1 minute). Excess water was removed by squeezing along and down the switch with a gloved hand.

Switches were combed through and a second Hellerman sleeve attached 20 cm from the first. Each switch was then placed in a petri dish and 1 gm of product applied between the sleeves.

The product was massaged into the switch using a gloved hand. The switches were then wound onto rollers under a tension of 100 g and placed into a drying cabinet for 1 hour at 50°C. They were then transferred to a humidity cabinet for equilibration at 20°C and 84% relative humidity. (The cabinet was located in a laboratory where the temperature was controlled.) Equilibration was normally carried out overnight and certainly for no

less than 12 hours. In the cabinet the switches were removed from the rollers and secured in position on a gridded chart. Readings were then taken as follows:

- 0 - 30 minutes, read at 5 minute intervals
- 30 - 60 minutes, read at 10 minute intervals
- 60 - 180 minutes, read at 20 minute intervals

A final reading was taken at 24 hours, or later if required.

Curl retention was then calculated according to the following equation:

$$\% \text{ curl retention} = \frac{L_0 - L_t}{L_0} \times 100$$

where  $L_0$  = original length  
 $L_0$  = length at time 0  
 $L_t$  = length at time t

#### Body

To investigate the delivery of tactile body to the hair and gain some indication of film flexibility the following paired comparison procedure was adopted. Six balanced Yugo Red Tie hair switches, 4 g, 10.5 cm, were washed thoroughly with 2 x 0.5 ml 12% (w/w) SLES 2EO. After rinsing and removal of excess water from the switch, 1 gm of product to be tested was applied to each of 3 switches, each switch being contained in a petri dish. The product was massaged into the switch using a gloved hand. The remaining 3 switches were treated with the comparative test material. The switches were then set onto 3 cm diameter PTFE rollers and placed in a drying cabinet at 50°C for 1 hour. Switches were allowed to cool at ambient temperature and humidity for at least 30 minutes before being removed from the roller for paired comparison evaluation. This involved

suspending appropriate pairs of switches and asking trained panellists to assess the curl which gave the greatest resistance to compression by squeezing between the thumb and forefinger. Prior to each panellist evaluation, the switches were combed thoroughly 5 times, the protocol for which was as follows: first comb over outside of switch; combs 2-4 over inside of switch; comb 5 over outside of switch.

#### Smoothness and Ease of Comb

To investigate the benefits of smoothness and ease of comb the following paired comparison procedure was carried out on SLES 2EO washed, balanced switches. Six Yugo Red Tie hair switches, 7 g, 25 cm, were dampened with tap water and any excess removed by squeezing along and down the switch with a gloved hand. 1 g of product was applied to each switch and massaged into the switch using a gloved hand. After product application the switches were hung vertically in a drying cabinet at 50°C for 1 hour. The switches were then removed and allowed to cool for at least 30 minutes. The switches were combed through until all the tangles were eliminated. For the paired comparison evaluation, pairs of treated switches were presented to the panellists who were asked to indicate their preference in terms of hair smoothness, by stroking each of the switches between their index and forefingers using one hand only.

After smoothness evaluation panellists were asked to comb through the switches and give their preference in terms of ease of comb. They were not allowed to comb any switch more than 3 times.

#### Example 1

A salt of chitosan with 2-hydroxyoctanoic acid (HCA) was prepared by the following method:

HCA (28.8 g, 0.18 mol) was dissolved in warm water (4l) to give a colloidal solution. The solution was cooled and glacial acetic acid (10.8 g, 0.18 mol) was added. Chitosan (68 g, 85% deacetylated Chitin, 0.18 mol; MW300,000) was added to this mixed acid solution. The initial particle suspension was then stirred until the Chitosan largely dissolved to give a viscous solution. This solution was filtered prior to use.

To assess the hair setting and conditioning properties of the chitosan-HCA salt, a series of comparative tests were conducted on hair switches for various attributes using as a comparative composition an aqueous solution of a conventional film-forming polymer, PVP/VA I535 (poly-N-vinyl pyrrolidone/vinyl acetate copolymer, ex GAF).

The chitosan-HCA salt was dissolved in distilled water to give a composition comprising 1% by weight of the salt. In a second test solution this concentration was halved to 0.5% by weight. The PVP/VA solution was made up in the same manner, but with the polymer being present in an amount of 3.5% by weight.

Each of the above test solutions of the chitosan-HCA salt and the solution of PVP/VA was tested for curl retention according to the protocol described above. The results were as follows:

	<u>Curl retention (%)</u>	
	<u>3 hours</u>	<u>24 hours</u>
Chitosan-HCA (1%wt)	98	93
Chitosan-HCA (0.5%wt)	94	88
PVP/VA I535 (3.5%wt)	83	57

The results clearly show that the chitosan-HCA salt, at varying concentrations, gives significantly superior curl retention than does PVP/VA, a conventional film-

forming polymer used in cosmetic products.

The 1%wt solution of chitosan-HCA salt and the solution of PVP/VA were subjected to a two thirds size paired comparison test for smoothness and ease of combing in accordance with the protocols described above. The first test (A) was followed by a second test (B) using new hair switches to test the reproducibility of the results. The results were as follows.

		<u>Voting split*</u>	
		<u>Chitosan-HCA</u>	<u>PVP/VA</u>
Smoothness	(A)	38	16
	(B)	50	4
Ease of Comb	(A)	41	13
	(B)	46	8

\* All the results were statistically significant at 95% confidence level.

The results show that the chitosan-HCA salt gives significantly superior hair smoothness and ease of combing than does PVP/VA, a conventional film-forming polymer used in cosmetic products.

CLAIMS:

1. A salt of chitosan or a chitosan derivative with one or more molecules of a hydroxycarboxylic acid having a carbon chain backbone with a length of at least 5 carbon atoms and containing at least one hydroxyl group.
2. A salt as claimed in claim 1, wherein the carbon chain backbone is linear or branched and has a length of from 5 to 30 carbon atoms.
3. A salt as claimed in claim 2, wherein the carbon chain backbone has a length of from 6 to 16 carbon atoms.
4. A salt as claimed in any one of claims 1 to 3 which contains from 1 to 5 hydroxyl groups.
5. A salt as claimed in claim 4 which contains from 1 to 3 hydroxyl groups.
6. A salt as claimed in claim 4 or claim 5, wherein the or at least one of the hydroxyl groups is in the 2-position relative to the carboxyl group of the acid.
7. A salt as claimed in any preceding claim, wherein the acid moiety is derived from a 2-hydroxyalkanoic acid.
8. A salt as claimed in claim 7, wherein the acid is 2-hydroxyoctanoic acid.
9. A salt as claimed in claim 1, which is a mixed salt comprising, in addition to the said hydroxycarboxylic acid having a carbon chain backbone with a length of at least about 5 carbon atoms and containing at least one hydroxyl group, at least one

additional acid moiety.

10. A salt as claimed in any preceding claim which is water-soluble.

11. A fibre conditioning and bodying/setting composition comprising at least one salt as claimed in any one of claims 1 to 10.

12. A composition as claimed in claim 11, wherein the salt is present in an amount of 0.1 to 40% by weight of the composition.

13. A composition as claimed in claim 11 or claim 12, further comprising at least one volatile solvent selected from water, alcohols and mixtures thereof.

14. A composition as claimed in any one of claims 11 to 13, further comprising at least one surfactant selected from anionic, nonionic, amphoteric and zwitterionic surfactants, and mixtures thereof.

15. A composition as claimed in any one of claims 11 to 14, further comprising an additional fibre conditioning agent.

16. A composition as claimed in any one of claims 11 to 15, further comprising an additional fibre bodying/setting agent.

17. A method of treating fibres to simultaneously condition them and give them enhanced body and hold, the method comprising treating the fibres with a composition as claimed in any one of claims 11 to 16.

18. A method as claimed in claim 17, wherein the fibres which are treated are hair fibres.



19. Use for treating fibres to simultaneously condition them and give them enhanced body and hold of a salt as claimed in any one of claims 1 to 10 or a composition as claimed in any one of claims 11 to 16.

20. The use as claimed in claim 19 which is for the treatment of hair fibres.

**Patents Act 1977****Examiner's report to the Comptroller under  
Section 17 (The Search Report)** - 25-

Application number

GB 9313 4

**Relevant Technical fields**

(i) UK Cl (Edition L ) C3U (UDE)

(ii) Int Cl (Edition 5 ) A61K; C08B

**Databases (see over)**

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

**Search Examiner**


K MACDONALD

**Date of Search**

23 SEPTEMBER 1993

Documents considered relevant following a search in respect of claims 1-20

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

Category	Identity of document and relevant passages <i>-26-</i>	Relevant to cl. 

### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

**THIS PAGE BLANK (USPTO)**